

**Further Studies of the Interaction of Carbonyl Compounds with
Organometallic Azides, the Novel Reaction of Benzoquinone with
Trimethylsilylazide**

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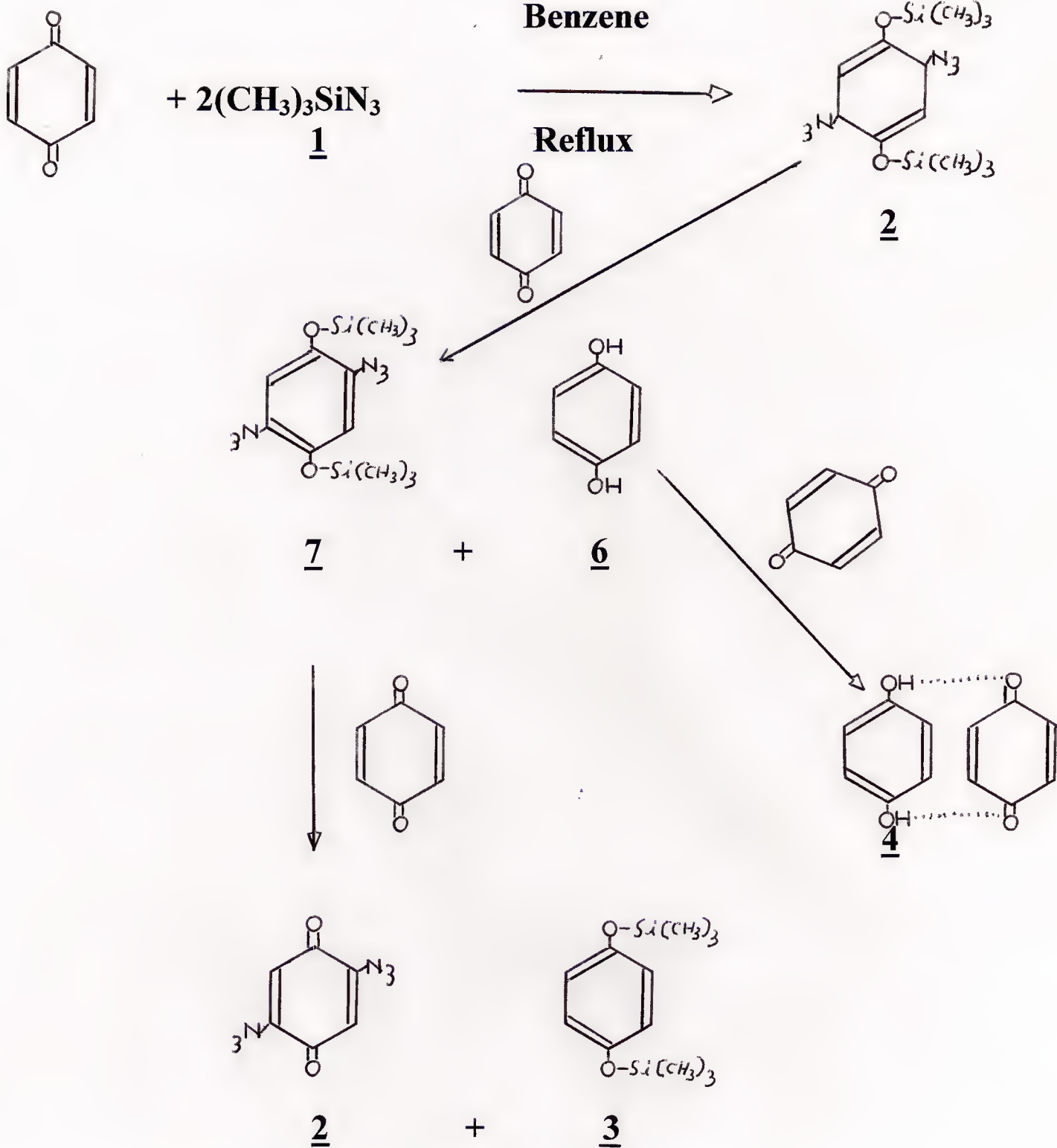
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Abstract:

Unlike the reaction of trimethylsilylazide (TMSA), (1), with maleic anhydride, which results in nitrogen ring insertion and production of "oxauracil" in high yield¹, reaction of TMSA with benzoquinone in warm non polar solvents gave a complex mixture of products, primarily 2,5-diazido benzoquinone, (2), 1,4-BIS-(trimethylsiloxy)benzene, (3), "quinhydrone", (4), the 1:1 adduct of hydroquinone, and hydroquinone (6). The results were postulated to involve rapid conjugate addition of 2 moles of TMSA to benzoquinone, yielding reactive intermediate bis-1,4-trimethylsiloxy, 3,6-diazido, 1,4-cyclohexadiene, (5). A rapid oxidation-reduction reaction of 5 with quinone yields hydroquinone (6) and bis-1,4-trimethylsiloxy-2,5-diazidobenzene (7). 6 further reacts in a similar fashion with benzoquinone yielding 4, while 7 further reacts with benzoquinone yielding 2 and 3. The reaction has limited synthetic utility due to the number of complex oxidation-reduction pathways available in this system.

PLATE 1



Procedure

A 25ml round bottom 3 neck flask equipped with a magnetic stirrer, 10ml dropping funnel, thermometer and nitrogen purge, was charged with 15ml benzene dried over molecular sieves and 5.4g (0.50 mol) re sublimed benzoquinone. The dropping funnel was charged with 7ml (0.050 mol) trimethylsilylazide (1). The mixture was stirred and heated to 45°C, whereupon all the benzoquinone dissolved. 1 was added drop wise over 0.5hr under nitrogen. A green solid precipitated and the solution turned deep red. The solid was suction filtered and dried, yielding 1.7g of quinhydrone (4), green crystals, mp 169°C, lit:² mp 169-172°C, UV lambda max (H₂O) 244,290 mu, lit:² 241, 290mu, IR (KBr) 3050(m), 1630(s), 1590(m),1460(s), 13609 (m), 1320(m), 1250(m), 1210(s),950 (w), 870(m), 840(m), 760(m) cm⁻¹. NMR (CDCl₃,100 MHz,) delta 6.61, 2H, (s), 6.71, 2H, (s) (aromatics, quinones), 7.61 (1H, (s), (OH). The IR and UV spectra were identical to those reported in ref 2. The material showed no melting point depression on admixture with an authentic sample of quinhydrone.

The red mother liquor from above was chromatographed on a 2 ft X 2 inch silica gel column with benzene eluant, yielding 0.39g red powder 2,5-diazido benzoquinone, (2), mp 88-90°C (dec) lit:³ 91°C (dec), IR (nujol) 2170, 2130, 1660, 1640, 1570, 1280, 1220, 880, 820, 760, 730 cm⁻¹ NMR (CDCl₃) 100 MHz, delta 6.21(s), identical to literature values ³. Further elution yielded 1.1 g 1,4-BIS (trimethylsiloxy)benzene, (3), mp 45-7°C, lit: mp 46°C, and 0.6 g hydroquinone (6), mp 170-171°C, lit:⁴ mp 170.5°C. Reactions run at temperatures above 45°C resulted in intractable black mixtures.

References:

- 1) S.S. Washburne, W.R. Peterson and D.A. Berman, J. Org. Chem., 37, 1738 (1972).
- 2) M.A. Slifkin and R.H. Walmsley, Spectrochim Acta, A, 1237, (1970).
- 3) H.W. Moore, H.R. Sheldon and D.F. Sheldon, J.O.C, 34, 1999, (1969).
- 4) Handbook of Chemistry and Physics, 4th Edition, p 1046.

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